The Chemisorbed State of Propene on Metals in Reference to the Catalytic Hydrogenation

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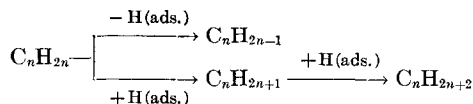
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The distributions of all the isotopic isomers of propene produced by its exchange reaction with deuterium oxide and by its hydrogenation reaction with D_2 have been investigated with the microwave absorption technique, and the following conclusions have been obtained, assuming that propane is produced via the half-hydrogenated state, C_3H_7, on nickel and palladium: (1) In both reactions catalyzed by nickel, the methine hydrogen of propene is the most exchangeable, and propene may be chemisorbed mostly as the undissociated C_3H_6(ads.) state, besides the half-hydrogenated state. (2) On palladium, however, all the hydrogens of three groups show nearly equal exchangeability, and some dissociated species, C_3H_5(ads.), may exist in addition to the above chemisorbed species. (3) Since water does not poison the formation of the half-hydrogenated state, it can supply such an amount of the chemisorbed hydrogen as can produce the half-hydrogenated state on the surface. Therefore, the exchange reaction can be regarded as a part of the hydrogenation.

INTRODUCTION

It is highly probable from the kinetic standpoint that a half-hydrogenated intermediate exists on metal surfaces in the catalytic hydrogenation of simple olefins, based especially on the study using deuterium as the isotopic tracer (*1*). In addition, existence of the dissociative chemisorbed state is proposed in the reaction scheme:

$$C_nH_{2n} \underbrace{\begin{array}{l} \xrightarrow{\;-H(ads.)\;} C_nH_{2n-1} \\ \xrightarrow{\;+H(ads.)\;} C_nH_{2n+1} \xrightarrow{\;+H(ads.)\;} C_nH_{2n+2} \end{array}}$$

Recently, Pliskin and Eischens (*2*) reported finding, by means of the infrared spectrometric method, the presence of alkyl and alkenyl species on nickel when ethylene is chemisorbed. This would give support to the above reaction scheme, but since only a physicochemical technique was used in the research, there remain other possible arguments against the above scheme, e.g., the reaction may proceed by direct addition of a hydrogen molecule to the chemisorbed olefin.

Such being the situation, it would be appropriate to apply a new technique to the present reaction, as will be introduced in this paper, and to obtain a new finding useful to the problem.
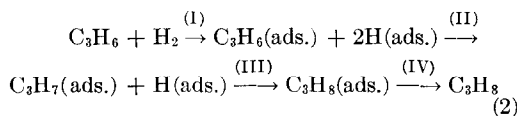
THEORETICAL

As mentioned already, the tracer method has been used extensively (*3*) on the hydrogenation of simple olefins so as to determine the distribution of deuterium in the product molecules, $C_nH_{2n+2-x}D_x(=d_x)$, where X ranges from 0 to $2n + 2$. As the analytical method for d_x, mass spectrometry was hitherto adopted and the results contributed much to the study of this problem, but even this method is insufficient to acquire any knowledge of the deuterium-substituted group in the product, i.e., the amount of various possible isomers cannot be determined on each d_x quantitatively. (Hereafter these isomers will be denoted by subspecies of d_x.) Therefore the chemisorbed state of the intermediates as well as the reaction scheme have not been determined finally.

According to our preliminary report (*4*), the microwave spectroscopic method has proved to be effective in analyzing all the subspecies of monodeutero-propene-d_1(CH$_2$DCH=CH$_2$, CH$_3$CD=CH$_2$, *trans*- and *cis*-CH$_3$CH=CHD), which are producible by the exchange reaction (1)

$$C_3H_6 + yD_2O \rightarrow C_3H_{6-y}D_y + yHDO \qquad (1)$$
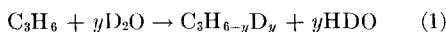
Now, if the scheme of the hydrogenation is expressed as follows:

$$C_3H_6 + H_2 \xrightarrow{(I)} C_3H_6(\text{ads.}) + 2H(\text{ads.}) \xrightarrow{(II)}$$
$$C_3H_7(\text{ads.}) + H(\text{ads.}) \xrightarrow{(III)} C_3H_8(\text{ads.}) \xrightarrow{(IV)} C_3H_8 \qquad (2)$$

the same technique may be applied to the study of the hydrogenation of propene, when deuterium is used instead of ordinary hydrogen, because the deuterium exchange reaction of propene proceeds as well as the addition reaction to propene [see reaction (3)],

$$C_3H_6 + D_2 \begin{cases} \rightarrow C_3H_{8-x}D_x\text{'s} & (3a) \\ \rightarrow C_3H_{6-y}D_y\text{'s} & (3b) \end{cases}$$
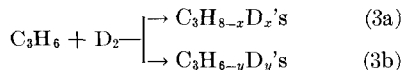
$$(x = 0, 1, \ldots 8; y = 0, 1, \ldots 6)$$

Generally, the formation of chemisorbed propane [step (III), reaction (2)] is regarded as rate-determining, i.e., the backward reaction of step (II) is as rapid in its rate as the forward one. This relationship ought to be expected by the present scheme. Therefore, when deuterium is used, various kinds of deuteropropene C$_3$H$_{6-y}$D$_y$($=d_y$) must be found in the reaction system in addition to the deuteropropanes ($=d_x$), if the reaction is not completed.

In the present report, the subspecies distribution of d_y in the "unreacted" propene obtained during the course of deuteration (3) is compared with the distribution obtained by the exchange reaction (1) utilizing the fact that the sensitivity of the microwave spectroscopy is high enough to determine the amount of deuteropropenes even if they are mixed with deuteropropanes.

Now, reaction (1) is, as is often done, considered to be a part of the reaction scheme (2), though the step (III) cannot be realized. Then, since the exchange occurs by the backward reaction of step (II), subspecies distribution of C$_3$H$_5$D($=d_1$) must be equal at the initial stage of both reactions. This assumption may be criticized because of the possibility that deuterium oxide plays the role of a kind of poison on the metal surface, judging from the fact that the rate of exchange is much smaller than that of the hydrogenation. However, this difference can be explained by the smaller concentration of chemisorbed hydrogen thermodynamically producible from water.

In order to carry out the above-mentioned attempt, it is convenient for discussion to compare the subspecies distribution of d_1 under the condition that the degree of deuterium exchange is nearly equal, and this condition will be adopted.

The investigation done from the above standpoint will contribute not only to answering the question of whether or not reaction (1) can be regarded as a part of the reaction (2), but will also yield knowledge of the chemisorbed state of simple olefins on metals. As the metal catalysts, nickel and palladium were selected, because these metals seem to represent the two extremes in such exchange reactions (*5*, *6*).

EXPERIMENTAL

Materials. Propene and deuterium gas (mass spectrometric analysis grade) obtained from Takachiho Industrial Co. were used without purification. No impurity was recognized by the gas chromatographic analysis in propene. Deuterium oxide obtained from Showa Denko K.K. (99.7%) was used without any purification. Nickel catalyst was prepared by decomposing commercial nickel formate (Mitsuwa Kagaku Kogyo K.K.) at 270°C and then was degassed at the same temperature for 20 hr. Palladium black obtained from Mitsuwa Kagaku Yakuhin Kogyo K.K. was reduced with hydrogen gas at 180°C, until no water was produced, followed by degassing at least 4 hr at the same temperature.

Procedure. The reaction was carried out by the static method; the reactants and catalyst were charged in glass ampuls of about 50 cc and 200 cc, respectively, for

reactions (1) and (3), and the ampuls kept at the reaction temperature. In order to stop reaction (3), the ampul was cooled with liquid nitrogen. After pumping off the part not condensable at that temperature, the remaining substance was subjected to analysis.

The d_y distribution of various deuteropropenes was determined by use of a mass spectrometer (Hitachi RMU-5), installed at the Institute of Protein Research, Osaka University. In order to avoid the overlapping of peaks of the deuteropropanes, the potential of the bombarding electron was made as low as possible. Abundances of various subspecies of d_1 and d_2 were determined by use of a microwave spectrometer with high sensitivity constructed at the Department of Chemistry, The University of Tokyo. The relative intensities of the $0_{00} \rightarrow 1_{01}$ transition (at 15–17 Gc/sec) were measured for each subspecies at Dry Ice temperature. The absorption cell was made of gold-plated copper, so that the reaction during the measurement could be neglected. Other details of the quantitative analysis have been already published (7).

For the sake of confirmation of the micro-

wave results, the products of reaction (1) were subjected to infrared spectrometry.

RESULTS

The experiment was carried out on palladium and nickel with respect to both reactions of hydrogenation (3) and exchange (1), as shown in Table 1. The reaction temperature was selected to be at room temperature, because an appreciable amount of the exchanged propene could be obtained only at or above this temperature, while the deuterated propanes could be produced at lower temperature (8). Other experimental conditions were kept as much the same as possible, and the reaction time was selected so as to stop the reaction at such a degree that the "unreacted" propene still remained in the reaction system, while the $\psi (= \frac{1}{6}\Sigma^6_{\nu=1} y d_\nu)$ value was made nearly equal, i.e., $\sim$8–12%. The amount of the consumed deuterium was estimated to be 85% and 80% in No. 4430 and No. 4806, respectively, judging from the pressure decrease. Among the five runs, No. 19-a, already reported (5), is added for the sake of discussion, because this run and No. 3315 show practically the same deuterium dis-

TABLE 1
EXPERIMENTAL CONDITIONS AND RESULTS

	No. 4430 (Pd, D_2)	No. 3315 (Pd, D_2O)	No. 4806 (Ni, D_2)	No. 3513 (Ni, D_2O)	No. 19-a (Ni, D_2O)
C_3H_6 (mmole)	2.18	2.18	2.18	2.18	2.18
D_2O (mmole)	—	10	—	10	10.5
C_3H_6/D_2 (in volume)	2.0	—	2.0	—	—
C_3H_6 (cm Hg)	10	—	10	—	—
Catalyst (g)	3.2_5	0.50	5.0	1.6_5	1.6_5
Temp. (°C)	20	25	20	17	25
Time	10.2 min	150 hr	6.9 min	25 hr	25 hr
d_0	$72._8$	$51._3$	$57._5$	$58._4$	$51._6$
d_1	$9._4$	$36._6$	$25._0$	$33._3$	$36._8$
d_2	$6._8$	$10._7$	$10._8$	$7._3$	$10._1$
d_3	$5._5$	$1._6$	$4._8$	$1._0$	$1._6$
d_4	$3._8$	—	$1._9$	—	—
d_5	$1._7$	—	—	—	—
d_6	—	—	—	—	—
$\psi = \frac{1}{6} \sum_{y=1}^{6} y d_y$ (%)	$7._7$	$10._4$	$11._6$	$8._5$	$10._5$

TABLE 2

SUBSPECIES DISTRIBUTION OF d_1

Run No.: System:	4430 Pd, D_2	3315 Pd, D_2O	4806 Ni, D_2	3513 Ni, D_2O
CH_2D—CH=CH_2[a]	54.0 ± 2.9 (18.0)	59.2 ± 2.2 (19.7)	36.2 ± 2.2 (12.1)	22.5 ± 2.7 (7.5)
trans-CH_3CH=CHD	16.4 ± 1.5	13.1 ± 1.3	11.4 ± 1.8	9.5 ± 2.1
cis-CH_3CH=CHD	13.4 ± 2.1	13.7 ± 1.5	11.7 ± 1.8	9.9 ± 2.2
CH_3CD=CH_2	16.1 ± 2.4	14.1 ± 1.3	40.7 ± 2.9	58.1 ± 5.1

[a] The CH_2D—CH=CH_2 subspecies are observed by microwave spectroscopy as two distinct species, but only the sum of their amount is listed in the table, because they can be regarded to be equivalent for the present research.

tribution and the same ψ value. Distribution of d_y values, shown in the lower part in the table, is slightly different between the runs of hydrogenation (Nos. 4430 and 4806) and the runs of exchange (Nos. 3315 and 3513). The former runs are wider in d_y distribution than the latter.

The analytical result with microwave spectroscopy,* shown in Table 2, was obtained on the samples without any separation of d_1 species from various other species of deuterated propanes and propenes. Nevertheless, the standard error of the data obtained was less than a few %, as shown in Table 2. The numerals in parentheses are those of CH_2DCH=CH_2 divided by 3, so as to obtain the exchange degree per one methyl hydrogen for the sake of comparison. The accuracy of determination on the subspecies of d_2 became slightly worse than on that of d_1.

The subspecies distribution of d_2 is not shown because it is unnecessary in the present paper. But it was taken up in a paper published (7) on samples No. 3315 and No. 3513, and statistical treatment of the exchange reaction was discussed, leading to the conclusion that each subspecies of d_2 is produced via a process independent of the subspecies distribution of d_1.

The infrared spectra of the products of No. 19-a and No. 3513 are shown in Fig. 1, which covers the region of C–D stretching bands. Since the shapes of the spectra are different, it is evident that the degree of deuterium exchange at the hydrogen of each

* The 0_{00}–1_{01} transition is shown in Fig. 4 of ref. (7).

group is qualitatively different between the Ni and the Pd catalyst, even if the ψ values are practically the same on both samples. Moreover, since the bands at 2161, 2170, and
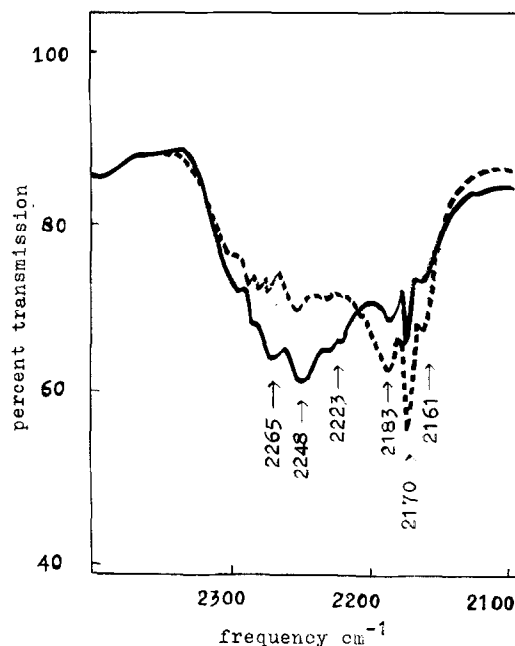

FIG. 1. IR spectra of Nos. 19-a (Ni) and 3315 (Pd): ———, No. 19-a (Ni); - - - - - No. 3315 (Pd); pressure of samples, 10 cm Hg, cell length, 13.5 cm.

2183 cm^{-1} can be assigned† to the C–D stretching of the methyl group and the bands at 2248 and 2265 cm^{-1} to those of the vinyl group, easier exchangeability of the vinyl hydrogen on nickel than on palladium is thus confirmed by infrared spectrometry.

† Concerning the assignment, see ref. (5).

However, the exchangeability of the three hydrogens in the vinyl group could not be evaluated separately without ambiguity by this method.

DISCUSSION

Distribution of Subspecies of d_1

Table 2 and Fig. 1 show evidence for the characteristic catalytic exchangeability of nickel and palladium toward hydrogen in propene. The difference lies in the exchange degree of three kinds of hydrogens, i.e., (a) methine hydrogen is the most exchangeable on nickel, (b) methyl hydrogen is slightly more exchangeable than both methylene and methine hydrogens on palladium, and (c) the exchangeability of the *trans* and *cis* hydrogens at the methylene group is practically the same on both metals.
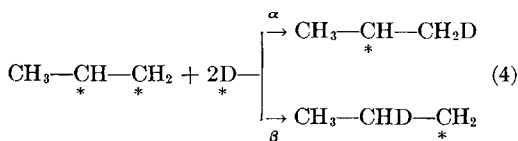
It is noteworthy that the above three tendencies are held in common by both the hydrogenation (3) and the exchange reactions (1), though the exchange rate per equal amount of palladium and nickel is, respectively, about 140 and about 650 times as small as the hydrogenation rate. This difference in rates may be explained by the concentration difference of the chemisorbed hydrogen, which can be produced by the neutralization of hydrogen ion with metal electrons. Therefore, the role of water as a catalytic poison to the metals, as mentioned above, may not be important as far as the formation of the half-hydrogenated state is concerned.

Mechanism on Nickel

A slight discrepancy shown in the subspecies distribution of d_1 between the reactions (1) and (3b) (cf. Nos. 3513 and 4806) must be noteworthy in comparison with a good coincidence in the case of palladium (cf. Nos. 4430 and 3315). This tendency on nickel can be explained if the chemisorbed propene dissociates partially and slowly in the case of the propene–deuterium system, since the amount of CH_2D—CH=CH_2 is larger in No. 4806 than in No. 3513. This tendency is plausible from the bond dissociation energies of C—H

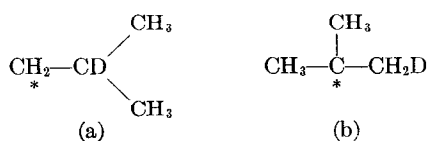(9): $D(CH_2CHCH_2 \rightarrow H) = 76.5$ kcal/mole and $D(CH_2CH \rightarrow H) = 104$ kcal/mole, respectively. This explanation means that water may poison the dissociation of chemisorbed propene.

The present authors (5) presented the following scheme as the mechanism of formation of the C_3H_7 species on nickel:

$$CH_3\text{—}CH\text{—}CH_2 + 2D\text{—}\begin{cases} \overset{\alpha}{\rightarrow} CH_3\text{—}CH\text{—}CH_2D \\[2mm] \overset{}{\underset{\beta}{\rightarrow}} CH_3\text{—}CHD\text{—}CH_2 \end{cases} \quad (4)$$

(* denotes the chemisorbed position)

However, the relative rates of both steps (α and β) could not be determined. Now, by use of the data of No. 4806 and No. 3513, the β step can be concluded to be the faster. The above conclusion is also plausible on the basis of the result obtained by Wilson *et al.* (10), who obtained no deuteroisobutene in the hydrogenation of isobutene with D_2 on nickel. This finding was explained by Siegel and Smith (11), who assumed the formation of the intermediate (a) rather than the intermediate (b) during deuteration. Taking this result into consideration, the state of the chemisorbed propene on nickel would be in equilibrium with the half-hydrogenated state, predominantly shown by the step (β) and its reverse.

$$\underset{(a)}{\underset{*}{CH_2}\text{—}CD\overset{\diagup CH_3}{\diagdown CH_3}} \qquad \underset{(b)}{CH_3\text{—}\underset{*}{\overset{\mid}{\underset{\mid}{C}}}\text{—}CH_2D}$$

The formation of CH_2D—CH=CH_2 can be explained by occurrence of the following process in parallel with the reverse process in reaction (4):

$$CH_3\text{—}\underset{*}{CH}\text{—}CH_2D \overset{-H}{\longrightarrow} \underset{*}{CH_2}\text{—}\underset{*}{CH}\text{—}CH_2D \quad (5)$$
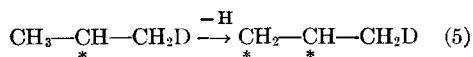
This is the reason why the distribution of deuterium is nearly equal among the five hydrogens in methyl and methene groups within experimental error in the case of nickel catalyst. Such an isomerization mechanism has been suggested in the former report (5).

Mechanism on Palladium

The above argument may not be applicable to the case of palladium, because this metal can adsorb hydrogen much more easily than nickel. This is the reason why better agreement of the subspecies distribution of d_1 was obtained between the runs on hydrogenation (No. 4430) and exchange (No. 3315), in spite of the different source of deuterium. If so, the rate-determining step of the hydrogenation on palladium may be concluded to be the step (III). Nevertheless, in order to assign finally the reaction scheme to (2), there remains a point to be discussed in more detail, because dissociation of propene may occur on palladium more easily than on nickel. This possibility, however, will not change the above conclusion if the equilibrium of dissociation is assumed on palladium, besides the equilibrium of C_3H_7 formation, as follows:

$$C_3H_7 \rightleftharpoons C_3H_6 + H \rightleftharpoons C_3H_5 + 2H \quad (6)$$
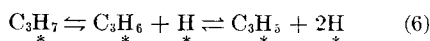
Now, the dissociative state of propene, $C_3\underset{*}{H_5}$, would be allowed to the palladium surface, on which even methyl hydrogen may be split off and adsorbed easily. This assumption may be supported by the subspecies distribution of d_1, i.e., the exchangeability of methyl hydrogen is larger per atom than that of methylene hydrogen, indicating that $CH_2D—CH=CH_2$ is also produced by some reaction scheme other than the isomerization scheme proposed on nickel.

Of course, from the energetic standpoint, the structure of the allyl type, $CH_2 \doteq CH \doteq CH_2$, may be more plausible than that of $\dot{C}H_2—CH=CH_2$ as the structure of C_3H_5. Formation of such an allyl species was experimentally concluded by Sachtler (12) on bismuth molybdate catalyst and by Voge et al. (13) on Cu_2O-Celite catalyst. However, the possibility that the $C_3\underset{*}{H_5}$ species is an intermediate π-bonded to the surface as proposed in the adsorption of alkanes (14, 15) will not be discussed now. This important problem of the nature of bonding is to be investigated in the future, as well as the further dissociation of $C_3\underset{*}{H_5}$. It is expected to be possible.

The above conclusion on the selectivity of nickel was already mentioned (5), while the conclusion for palladium will be confirmed in the next paper from the kinetic standpoint.

Finally it might be mentioned that further investigation is now going on, in order to investigate in more detail the reaction mechanism, especially by use of the distribution of highly deuterated propenes produced in the reactions.

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